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DIELECTRIC RELAXATION OF LIQUIDS CONTAINING POLAR MOLECULES WITH ROTATING GROUPS

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ABSTRACT. The theory of dielectric relaxation, in an alternating electric field of angular frequency ω of liquids composed of polar molecules with rotating groups has been developed on the basis of rotational jumps of dipolar molecules across potential barriers. Expressions for the average dipole moment and the complex dielectric constant (ϵ^*) have been deduced and equations showing the explicit dependence of ϵ' and ϵ'' on the angular frequency and on the times of relaxation have been obtained. The applicability of these equations to the determination of the times of relaxation of the whole polar molecule and of the rotating polar group in the case of polar liquids and very dilute solutions of polar compounds in non-polar solvents has been discussed.

INTRODUCTION

The theory of anomalous dispersion of electric waves in polar liquids with rigid dipolar molecules on the basis of rotational Brownian motion was given by Debye (1929). This theory was extended by Budo (1938) to the case of polar molecules having a number of rotatable polar groups attached to the molecular frame. Frenkel (1946) pointed out that the notion of rotational Brownian motion is applicable to large molecules but is inadequate for liquids comprising small molecules which generally change their orientations sharply. Kauzmann (1942) developed the theory of dielectric relaxation on the basis of rotational jumps of dipoles across potential barriers and obtained the Debye equation both when those jumps are large and small. It appears that the theory is applicable to polar liquids composed of rigid dipoles only and as such is not applicable to polar liquids whose molecules have one or more rotatable polar groups attached to them.

In the present paper Kauzmann's theory has been applied to the latter type of polar liquids and as a typical example the case of liquid anisole has been considered.

THEORY

a) *Determination of the probability density of dipole distribution*

Consider a volume of liquid composed of anisole molecules at a certain temperature $T°K$. In the volume of the liquid imagine a system of fixed cartesian co-ordinates OXYZ of which the Z-axis defines the direction of the electric field (when there is one) and the origin O is at the centre of gravity of the electric charge

distribution in the molecule. The Z-axis is contained in the plane of the phenyl ring of the anisole molecule so that the orientation of the axis of rotation of the methoxy-group, the $C—O$ bond, is defined by the polar angles θ and ϕ as shown in figure 1.

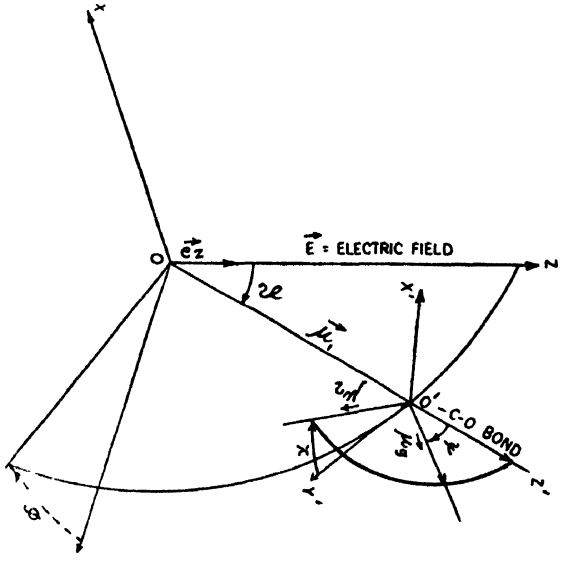

Figure 1.

Also imagine another system of co-ordinates O'X'Y'Z' rotating with the molecule in which the origin O' is at the C-atom of the $C—O$ bond and the bond itself defines the direction of Z' axis. The Y'-axis is in the plane of the phenyl ring (ϕ = const) and the X—axis is at right angles to it. In this frame the position of μ_g, the moment of the rotating OCH_3-group is given by the angles ψ and χ (figure 1) while ψ is fixed by the geometry of the molecule, χ varies between 0 and π, corresponding to the two extreme positions of equilibrium of μ_g. The observed moment μ of anisole molecule consists of two components—the fixed component μ_1 along the $C—O$ bond and the rotating component μ_2 at right angles to it. The moment μ_1 is composed of the moment $\mu_g \cos\psi$, μ_s-the moment of a rigid substituent in the para-position (if any) and μ'-any mesomeric moment as suggested by Grubb and Smyth (1961), while $\mu_2 = \mu_g \sin\psi$. Thus the total moment vector $\vec{\mu}$ of anisole is written as $\vec{\mu} = \vec{\mu}_1 + \vec{\mu}_2$ and its magnitude is given by $\mu^2 = \mu_1^2 + \mu_2^2$.

In the absence of any electric field at a certain temperature $T°K$ the molecules of anisole are at any instant in the average equilibrium positions determined by the intermolecular, potential energy V_1 (K cal/mole) due to the neighbouring molecules. The orientations of the axis of rotation of the methoxy-group i.e. the $C—O$ bonds in the molecules are distributed with a certain probability density denoted by f_1^0 and satisfying the relation $\int f_1^0 d\Omega = 1$ where f_1^0 may be a function

of θ and ϕ and $d\Omega = \sin\theta d\theta d\phi$. Due to the fluctuation of temperature within the liquid some molecules will acquire energy greater than V_1 and they would change their orientations with a probability $K_1^0 \propto e^{-V_1/KT}$. According to the principle of detailed balancing at equilibrium the number of molecules changing their orientations in a certain way will be equal to those following the reverse path. As a result the probability density is a constant and is given by $f_1^0 = 1/4\pi$.

On the other hand the distribution of the methoxy-group in the various molecule will be given according to Boltzmann distribution by the probability density function $f_2^0 = Ae^{-V_2(\chi)/KT}$ where $V_2(\chi)$ is the hindering potential with a barrier height of V_2 K cal/mole and also $\int_0 f_2^0 d\chi = 1$. Due to temperature fluctuations whenever the methoxy-group acquires energy greater than V_2 it would change its angular position with a probability $K_2^0 \propto e^{-V_2/KT}$. As in the previous case the direct and the reverse transitions occur with equal probability.

Now it is assumed that the above two processes by which the molecular dipoles change their orientations are independent of each other so that the joint probability density f^0 defining the distribution of the molecular dipoles is given by $f^0 = f_0^1 f_0^2$ and $\int f^0 \, d\Omega d\chi = 1$.

Let an alternating external electric field of amplitude E_0 and angular frequency ω represented by $\vec{E} = \vec{e_z} E_0 e^{j\omega t}$ be established in the OZ-direction, e_z being a unit vector in the direction of the Z-axis. The internal field acting on a molecule in the liquid will be giving by $\vec{F}$ which is related to $\vec{E}$ by Lorentz or Onsager relations. In the presence of the electric field the dipoles with different orientations will have different potential energies $-(\vec{\mu}.\vec{F})$ and consequently transitions to orientations with lower energy will be more favoured. There will be a slight excess of dipoles in the direction of the field and the liquid will show some overall polarisation. This is expressed mathematically by noting that the transition probabilities K_1^0 and K_2^0 in the field direction will be increased and those against the field will be diminished. Accordingly the probability densities f_1^0 and f_2^0 in favour of the field direction will increase slightly at the expense of those against the field. Since the interaction energies are small and vary with time the changes in the probability densities will also be small and time dependent.

Following Kauzmann (1942) and Van Vleck and Weisskopf (1945), the transition probabilities in the presence of the field are written as,

$$K_1(\theta\phi \rightarrow \theta'\phi' t) = K_1^0\left(1 - \frac{u'}{kT}\right) \qquad \ldots (1)$$

and

$$K_2(\chi \rightarrow \chi', \, t) = K_2^0\left(1 - \frac{v'}{kT}\right)$$

u' and v' are the potential energies of the final configurations in the two cases. These quantities are easily obtained as

$$u = -\mu_1 F_0 e^{j\omega t} \cos\theta \text{ and } v = \mu_2 F_0 e^{j\omega t} \sin\theta \cos\chi.$$

The perturbed probability densities in the presence the field will be given by $f_1 = f_1^0 (1+g_1)$ and $f_2 = f_2^0 (1+g_2)$ where g_1 and g_2 are time dependent small quantities which are functions of θ, χ and t . The joint probability density is given by $f = f_1 f_2$ and $\int\int f d\Omega d\chi = 1$.

We shall now calculate f_2 under the assumption that the position of the axis of rotation is held fixed at the angles θ and ϕ while the OCH_3 group turns from χ to χ' or χ to χ.

Following Kauzmann (1942) the time variation of f_2 written as

$$\frac{df_2}{dt} = -\int_0^\pi f_2(\chi, t) K_2(\chi \rightarrow \chi', t) d\chi' + \int_0^\pi f_2(\chi', t) K_2(\chi' \rightarrow \chi, t) d\chi' \quad .. \quad (3)$$

using the expressions for $f_2(\chi, t)$, $K_2(\chi \rightarrow \chi', t)$ etc., from equations (1) and (2) and noting that $v(\chi) = \mu_2 \sin\theta \cos\chi F_0 e^{j\omega t}$ we get from equation (3) after neglecting terms which are products of two first order quantities,

$$f_2^0 \frac{dg_2}{dt} = -\pi K_2^0 f_2^0 (1+g_2) + K_2^0 - \frac{K_2^0 v(\chi)}{KT} + \frac{f_2^0 K_2^0}{KT} \int_0^\pi v(\chi') d\chi$$

$$+ K_2^0 \int_0^\pi f_2^0(\chi') g_2(\chi') d\chi' \quad .. \quad (4)$$

The fourth term on the right hand side expression of equation (4) is zero for $\int_0^\pi \cos\chi' d\chi' = 0$ and the last term also vanishes because,

$$\int_0^\pi f_2^0(\chi') d\chi' = 1 = \int_0^\pi f_2(\chi') d\chi' = \int_0^\pi f_2^0(\chi') d\chi' + \int_0^\pi f_2^0(\chi') g_2(\chi') d\chi'.$$

whence $$f_2^0 \frac{dg_2}{dt} = K_2^0 (1 - \pi f_2^0) - \pi K_2^0 f_2^0 g_2 - \frac{K_2^0 v(\chi)}{KT} \quad .. \quad (5)$$

The steady state solution of equation (5) is obtained, by assuming $g_2 = g_0 + g_t$ where g_0 is the part independent of time and $dg/dt = j\omega g_t$, g_t being the time dependent part, as

$$f_2^0 g_2 = \frac{1}{\pi} - f_2^0 - \frac{K_2^0}{KT} \frac{v(\chi)}{j\omega + \pi K_2^0} \quad .. \quad (6)$$

and $f_2 = f_2^0 + f_2^0 g_2$ is given by,

$$f_2 = \frac{1}{\pi}\left[1 - \frac{\mu_2 F_0 e^{j\omega t}}{KT} \frac{\sin\theta\cos\chi}{1+j\omega\tau_2}\right] \tag{7}$$

where the expressions for $v(\chi)$ and $\tau_2 = 1/\pi K_2^0$ have been used.

In a similar manner, when the position of μ_g is kept fixed, we find for f_1 the expression,

$$f_1 = \frac{1}{4\pi}\left[1 + \frac{\mu_1 F_0 e^{j\omega t}}{KT} \frac{\cos\theta}{1+j\omega\tau_1}\right] \tag{8}$$

with $$\tau_1 = \frac{1}{4\pi K_1^0}$$

The joint probability $f = f_1 f_2$ is then written down as the products of the expressions in equations (7) and (8). Neglecting the second order small terms f is given by

$$f = \frac{1}{4\pi^2}\left[1 + \frac{F_0 e^{j\omega t}}{KT}\left(\frac{\mu_1\cos\theta}{1+j\omega\tau_1} - \frac{\mu_2\sin\theta\cos\chi}{1+j\omega\tau_2}\right)\right] \tag{9}$$

b) Calculation of average moment :

The average value of the total moment vector $\vec{\mu} = \vec{\mu_1} + \vec{\mu_2}$ in the field direction is obtained from the relation $(\mu)_{av} = \int\int (\vec{\mu}.\vec{e_z}) f d\Omega d\chi$.

The above integration at once yields

$$(\mu)_{av} = \frac{F_0 e^{j\omega t}}{3KT}\left(\frac{\mu_1^2}{1+j\omega\tau_1} + \frac{\mu_2^2}{1+j\omega\tau_2}\right) \tag{10}$$

This expression is the same as deduced by Budo (1938).

It has already been remarked that the methoxy-group will change its orientation if the energy acquired by it through temperature fluctuations in the liquid is greater than the hindering potential V_2. If V_2 is large, then only in a fraction t of all molecules, the methoxy-group is capable of rotation and in the remaining $(1-t)$ fraction, the molecules orient as rigid dipoles of moment μ. Under these conditions the average value of the dipole moment will be modified to,

$$(\mu')_{av} = \frac{F_0 e^{j\omega t}}{3KT}\mu^2\left[t\left(\frac{\mu_1^2}{1+j\omega\tau_1} + \frac{\mu_2^2}{1+j\omega\tau_2}\right) + \frac{(1-t)\mu^2}{1+j\omega\tau_1}\right] \quad .. \quad (11)$$

since $\mu^2 = \mu_1^2 + \mu_2^2$ we obtain from the above equation

$$(\mu')_{av} = \frac{F_0 e^{j\omega t}}{T}\mu^2\left(\frac{C_1}{1+j\omega\tau_1} + \frac{C_2}{1+j\omega\tau_2}\right) \tag{12}$$

with $C_1 = 1-\frac{t\mu_2^2}{\mu^2}$, $C_2 = \frac{t\mu_2^2}{\mu^2}$ and $C_1+C_2 = 1$.

c) *Derivation of the expressions for ϵ' and ϵ''*

From equation (12) the orientational polarisability per molecule which equals the average dipole moment per unit applied external field is then written as,

$$\frac{\mu^2}{3KT}\left(\frac{C_1}{1+j\omega\tau_1}+\frac{C_2}{1+j\omega\tau_2}\right)\cdot\frac{\vec{F}}{\vec{E}} \qquad (13)$$

If the Lorentz internal field $\vec{F} = \frac{\epsilon^*+2}{3}\vec{E}$ is used ϵ^* being the complex dielectric constant $= \epsilon'-j\epsilon''$, the following relation is obtained with the help of equation (13),

$$\frac{\epsilon^*-1}{\epsilon^*+2}\cdot\frac{M}{\rho} = \frac{4\pi N}{3}(\alpha_e+\alpha_{or}) \qquad (14)$$

where α_e is the polarisability at extremely high frequency, M/ρ the molar volume and N the Avogadro's Number. Using similar expressions for ϵ_0 the dielectric constant for static field ($\omega\sim 0$) and ϵ_0 the dielectric constant for extremely high frequency ($\omega\sim\infty$) in conjunction with equation (14) we obtain,

$$\frac{\epsilon^*-\epsilon_\infty}{\epsilon_0-\epsilon_\infty}\cdot\frac{\epsilon_0+2}{\epsilon^*+2} = a-jb \qquad .. \quad (15)$$

where $a = \frac{C_1}{1+\omega^2\tau_1^2}+\frac{C_2}{1+\omega^2\tau_2^2}$ and $b = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2}$ .. (16)

Further simplification of equation (15) and sorting out of real and imaginary terms gives,

$$\left.\begin{aligned}\epsilon'(s-a)+b\epsilon'' &= 2a+s\epsilon_\infty\\ \text{and}\quad \epsilon''(s-a)-b\epsilon' &= 2b\end{aligned}\right\} \qquad s = \frac{\epsilon_0+2}{\epsilon_0-\epsilon_\infty} \qquad .. \quad (17)$$

From equation (17) the expressions for ϵ' and ϵ'' are obtained as,

$$\left.\begin{aligned}\frac{\epsilon'-\epsilon_\infty}{\epsilon_0-\epsilon_\infty} &= \frac{a\beta-(a^2+b^2)(\beta-1)}{(a^2+b^2)(\beta-1)^2-2a\beta(\beta-1)+\beta^2}\\ \text{and}\quad \frac{\epsilon''}{\epsilon_0-\epsilon_\infty} &= \frac{b\beta}{a^2+b^2)(\beta-1)^2-2a\beta(\beta-1)+\beta^2}\end{aligned}\right\} \qquad .. \quad (18)$$

where $\beta = \frac{s}{s-1} = \frac{\epsilon_0+2}{\epsilon_\infty+2}$

Alternatively, we have the relations,

$$\left.\begin{aligned} a &= \frac{(\epsilon_0+2)\{(\epsilon'-\epsilon_\infty)(\epsilon'+2)+\epsilon''^2\}}{(\epsilon_0-\epsilon_\infty)\{(\epsilon'+2)^2+\epsilon''^2\}} \\ \text{and} \quad b &= \frac{(\epsilon_\infty+2)(\epsilon_0+2)\epsilon''}{(\epsilon_0-\epsilon_\infty)\{(\epsilon'+2)^2+\epsilon''^2\}} \end{aligned}\right\} \quad .. \quad (19)$$

Since ϵ'' is small ϵ''^2 may be neglected, and equation (19) gives

$$\left.\begin{aligned} a &= \frac{\epsilon'-\epsilon_\infty}{\epsilon_0-\epsilon_\infty} \cdot \frac{\epsilon_0+2}{\epsilon'+2} \\ \text{and} \quad b &= \frac{\epsilon''}{\epsilon_0-\epsilon_\infty} \cdot \frac{(\epsilon+2_\infty)(\epsilon_0+2)}{(\epsilon'+2)^2} \end{aligned}\right\} \quad .. \quad (19a)$$

While equations (18) gives the explicit dependence of ϵ' and ϵ'' on ω or τ_1 and τ_2, it will be easier in practice to use the relations in equations (19) or (19a). for obtaining the τ_1 and τ_2-values from measurements on ϵ' and ϵ'' at different frequencies It may be noted that for some pure liquids and very dilute solutions of polar compounds in non-polar solvents for which $\epsilon_0 \approx \epsilon' \approx \epsilon_\infty$, equations (18) and (19) give the same relations for ϵ' and ϵ'' viz.,

$$\left.\begin{aligned} \frac{\epsilon'-\epsilon_\infty}{\epsilon_0-\epsilon_\infty} &= a = \frac{C_1}{1+\omega^2\tau_1^2}+\frac{C_2}{1+\omega^2\tau_2^2} \\ \text{and} \quad \frac{\epsilon''}{\epsilon_0-\epsilon_\infty} &= b = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2} \end{aligned}\right\} \quad .. \quad (20)$$

Many workers have used the simpler relations of equation (20) for obtaining τ_1 and τ_2 in the case of polar liquids where the approximations $\epsilon_0 \approx \epsilon' \approx \epsilon_\infty$ do not hold and consequently the τ-values so determined will be erroneous.

For very dilute solutions of polar molecules in non-polar solvents in the limiting case of vanishing concentration the expression for loss-tangent, tan δ is obtained from equation (20) easily, by substituting the value of $\epsilon_0-\epsilon_\infty$

$$\tan\delta = \frac{\epsilon''}{\epsilon'} = \epsilon_i \frac{-\epsilon_\infty}{\epsilon'} \cdot b = \frac{4\pi NC\mu^2}{27KT} \frac{(\epsilon_\infty+2)(\epsilon_0+2)}{\epsilon'} \cdot b \quad .. \quad (21)$$

where ϵ_0 and ϵ_∞ respectively, are the static and very high frequency dielectric constants of the solution and C is the concentration of the solute in moles per c.c. In the case of vanishing concentration we get for incremental tan δ i.e. $\Delta(\tan\delta)$ (since $\epsilon_0 \approx \epsilon' \approx \epsilon_\infty$ the static dielectric constant of the solvent, $\sim \epsilon_0$) the expression,

$$\Delta(\tan\delta) = \underset{C\to 0}{Lt} \frac{\partial}{\partial C}(\tan\delta) = \frac{4\pi N\mu^2}{27KT} \frac{(\epsilon_0+2)^2}{\epsilon_0} b \quad (22)$$

and for small concentrations, $\tan\delta = C.\Delta(\tan\delta)$ or

$$\frac{T\tan\delta}{C}\Big/\frac{4\pi N\mu^2}{27K}\frac{(\epsilon_0+2)^2}{\epsilon_0} : b = \frac{C_1\omega\tau_1}{1+\omega^2\tau_1^2}+\frac{C_2\omega\tau_2}{1+\omega^2\tau_2^2} \quad .. \quad (23)$$

CONCLUSION

In conclusion it may be pointed out that in the case of very dilute solutions of anisole in non-polar solvents it has not been possible to detect experimentally any significant variations in the a and b values obtained from the exact equation (19) or from the approximate equation (20). Consequently the values of τ_1 and τ_2 determined from either sets of equations are practically the same. However, in the case of pure polar liquids e.g. anisole and phenetole, the values of a at different temperatures calculated from equation (20) are 10-20% lower than those obtained from equation (19) while the b-values obtained from the former equation are 15-25% higher than those obtained from latter equation. Some experimental results on the dielectric relaxation of anisole in very dilute solutions in different non-polar solvents at different temperatures (Kastha *et al*, 1967) have been published. Similar results with anisole and phenetole in the liquid state are in the course of publication.

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